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Correlations among Miscibility, Structure and Properties in Thermoplastic Polymer/Lignin Blends

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Abstract

Blends were prepared from an industrial lignosulfonate and seven matrix polymers with different chemical structures. The components were homogenized in an internal mixer and plates were compression molded for further testing. The blends were characterized by a number of methods: structure by scanning electron microscopy, interactions by dynamic mechanical thermal analysis and differential scanning calorimetry, while mechanical properties by tensile testing. Only weak dispersion forces develop in polyolefins, the properties of the blends are poor. Aromatic, π electron interactions are stronger and H-bonds result in reasonable compatibility and mechanical properties. The best properties were achieved with the ionomer as matrix in which the combination of hydrogen bridges and ionic bonds result in good compatibility and properties. The strength of interactions was estimated with the Flory-Huggins interaction parameter and good quantitative correlations were found among miscibility, structure and properties, which could be predicted with simple theories. Although blends with acceptable properties could be prepared from the ionomer and lignin, the deformability of most blends were very small limiting practical application. The plasticization or chemical modification of lignin may lead to materials which can be used in industrial practice.

Keywords: lignin blends, interactions, hydrogen bridges, ionic bonds, miscibility, compatibility, dispersed structure, modeling

Introduction

After cellulose, lignin is the second most abundant natural polymer produced by nature. Lignocellulosic plants contain it in various amounts from 17 to 33 % of their weight.¹ Lignin is produced as a byproduct in several technologies from cellulose to bioethanol production. Most of the lignin is burned during the production of cellulose by the Kraft process, but considerable amounts of lignin produced with the sulfite process find various, usually niche applications like additive for concrete,^{2,3} dispersing agent,⁴ adhesive,⁵ raw material for the production of chemicals,^{6,7} etc. The increasing environmental awareness of the public drives researchers towards finding value added applications for lignin, which might replace depleting fossil fuel resources and improve the carbon footprint of the economy. An obvious way to utilize lignin in the plastics industry is to use it as the component of a reactive resin or simply to blend it with other synthetic or biopolymers.⁸⁻¹¹

The source and the extraction technology of lignin affect considerably its structure; thus the type of lignin refers to these two factors. We can differentiate softwood and hardwood lignin, as well as Kraft lignin, liginosulfonate, organosolv lignin etc. The distinct chemical structure and interactions of these products are clearly demonstrated by the fact that liginosulfonate is soluble in water at any pH, while Kraft lignin can be dissolved only under alkaline conditions [12]. The cause behind this difference can be related to the presence of sulfonate groups in liginosulfonates. Nevertheless, other functional groups are very similar in all lignins, and pH does not play a role in polymer blends anyway. Therefore, whenever lignin is mentioned in our work, we mean liginosulfonate under the term and use lignin only for the sake of brevity.

The chemical structure of lignin is complicated, it is assumed as a highly branched or cross-linked substance partly grafted to hemicellulose chains. It contains numerous functional groups

including aliphatic and phenolic hydroxyls, carbonyl and carboxyl groups, and depending on the extraction technology functional groups with strong polarity like sulfonates in lignosulfonates.^{10,12} The functional groups offer possibilities to use lignin for various purposes or to modify them by chemical reactions.¹²⁻¹⁷ Many attempts were made to use lignin as stabilizer in polymers utilizing the hydrogen scavenging ability of its phenolic hydroxyl groups. Lignin stabilized the polymers in smaller and larger extent indeed, but its industrial utilization is difficult because of its limited efficiency compared to commercial phenolic antioxidants, strong smell and intensive color.^{10,18} The functional groups of lignin can develop interactions with all kinds of polymers but also very strong self-interactions making blending difficult.

Blends were prepared from lignin and many types of polymers, and the conclusions about the structure and properties of these blends are very controversial. Polyolefins are obvious choices as matrix for lignin blends,¹⁹⁻²⁷ but lignin was combined also with polystyrene,^{19,28,29} poly(ethylene terephthalate),^{20,29} polycarbonate,²⁹ poly(vinyl chloride),^{30,31} poly(vinyl alcohol),^{24,32} various biopolymers, like poly(lactic acid),³³⁻³⁶ polycaprolactone,³⁷ poly(hydroxybutyrate),³⁸ starch^{39,40} and proteins.^{41,42} Quite surprisingly, a wide variety of behaviors was reported for the blends from complete miscibility^{19,20,27,33,40-42} to complete immiscibility^{20,22-32,34-38} for all kinds of polymers. This is valid even for polyolefins,^{19,20,22-27} which is very strange in view of their apolar structure and lack of functional groups. Systematic research carried out with polymers with increasing polarity from polypropylene,²² to polymers forming aromatic, π -electron interactions,²⁹ hydrogen bonds²⁴ or electrostatic interactions⁴³ showed that interactions play a crucial role in the determination of the structure and properties of the blends. Complete miscibility was not observed in any of the cases, but lignin was dispersed in the form of droplets in the matrix polymer. The size of the particles changed with the strength of interactions and properties changed accordingly.

Obviously, the self-interactions of lignin molecules prevent miscibility, but competitive interactions with the functional groups of the matrix polymer lead to changing structure and properties.

Earlier studies focused either on a specific polymer or on specific interactions (dispersion forces, aromatic interactions, H-bond), but the latter were rarely determined or estimated quantitatively. We are not aware of any papers that compare interactions in various polymers and draw conclusions about their role in the determination of the structure and properties of polymer/lignin blends. Accordingly, the goal of this work was to use data collected in our previous projects,^{22,24,29,43} as well as to prepare blends from additional polymers and compare the results in order to draw general conclusions about the role of interactions in polymer/lignin blends. Component interactions are estimated quantitatively and correlations are established between interactions and structure, as well as between structure and properties. The perspectives of preparing blends with acceptable properties from polymers and lignin, as well as practical consequences are discussed in the final section of the paper.

Experimental

Materials

The type, source and most important characteristics of the polymers used in the experiments are summarized in **Table 1**. The polypropylene (PP) applied was the Tipplen H 649 FH grade homopolymer supplied by the MOL Group Ltd., Hungary. The polystyrene (PS, Styron 686 E) was supplied by Americas Styrenics, the polycarbonate (PC, Makrolon 2658) by Covestro and the glycol modified poly(ethylene terephthalate) (PETG, Ecosen SE) by SK Chemicals. The poly(methyl methacrylate) sample (PMMA, Altuglas HFI 7 Clear 101) was obtained from

Arkema, while the poly(lactic acid) (PLA) used was the Ingeo 4032 grade of NatureWorks. The ionomer (ION) applied was the Surlyn 1706 grade of DuPont, an ethylene-methacrylic acid copolymer partially neutralized by zinc hydroxide. The molecular mass of PP, PS, PC, PMMA and PLA was determined by gel permeation chromatography in trichlorobenzene (PP) or tetrahydrofuran (PS, PC, PMMA, PLA), respectively, while that of PETG by the measurement of intrinsic viscosity at 25 °C in 1,1,2,2-tetrachloroethane using the Mark-Houwink constants $K = 0.000372$ and $a = 0.73$.⁴⁴ The lignosulfonate sample used in the experiments was kindly supplied by the Burgo Group SpA, Italy. The Bretax C grade is derived from soft wood and it is the primary product of cellulose production. The counterion of the sulfonate groups is calcium. The lignin has small molecular mass (1400-2400 g/mol), and it contains various amounts of inorganic salts and sugar, i.e. reductive monosaccharides forming from cellulose and hemicellulose during the production of lignin. Whenever in further discussion lignin is mentioned, we always mean lignosulfonate under this term. The amount of lignin increased from 0 to 70 vol% in 10 vol% steps in the blends. Occasionally, blends with larger lignin contents could not be prepared because their viscosity was too large or the blends became too brittle to produce specimens from them.

Table 1 The most important characteristics of the polymers used as matrix materials in the experiments; identification, properties and chemical composition

Polymer	Density (g/cm ³)	MFR ^a (g/10 min)	M _n (g/mol)	M _w /M _n
PP	0.90	2.5	92600	4.84
PS	1.05	2.5	128000	2.44
PMMA	1.17	11.0	43500	1.88
PLA	1.24	3.9	24700	2.07
PC	1.20	13.0	88500	1.80
PETG	1.27	10.9	25000 ^b	—
Ionomer	0.95	0.7	—	—

a) melt flow rate at various temperatures and loads; b) calculated from intrinsic viscosity

Sample preparation

The components were homogenized in a Brabender W 50 EHT internal mixer at 42 cm³ charge volume, set temperature of 190 °C, rotational speed of 42 rpm and a mixing time of 10 min after the addition of lignin. PLA and PLA/lignin blends were processed at 180 °C, while PC and PC/lignin blends at 220 °C. Some polymers were dried before mixing (PLA at 110 °C for 4 hours, PC at 120 °C for 4 hours, PETG at 80 °C for 3 hours, and lignin at 120 °C for 72 hours), while the others were used as received. Torque and temperature were recorded during mixing and used in further analysis. After homogenization, plates of 1 mm thickness were compression molded at the temperature of homogenization using a Fontijne SRA 100 machine. Tensile bars were machined from the plates for further testing after storing them for one week at room temperature.

Characterization

In order to determine relaxation transitions and the glass transition temperature of the matrix polymer, dynamic mechanical thermal analysis (DMTA) was carried out on specimens with

50 x 5 x 1 mm dimensions between -150 °C and the melting or softening point of the sample at 1 Hz frequency, 10 µm deformation and 2 °C/min heating rate. Transitions were studied also by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7 apparatus. The measurements were done in two heating and one cooling runs between 30 °C and 220 °C with heating and cooling rates of 10 °C/min. The weight of the samples was 3-5 mg in each case. Mechanical properties were characterized by tensile testing using an Instron 5566 universal testing machine. Tensile bars were cut from the compression molded plates. Their shape and dimensions are given in **Figure S1** and **Table S1** of the Supplementary Information. Gauge length was 80 mm and the test was done at 10 mm/min crosshead speed. The structure of the blends was analyzed by scanning electron microscopy (SEM) using a Jeol JSM 6380 LA apparatus. Thin slices of 50-100 µm thickness were cut from the 1 mm thick plates using a Leica EM UC6 microtome and then the lignosulfonate was completely removed from the slices by dissolving it in distilled water in 24 hours at ambient temperature. Before taking the micrographs, the slices were coated by sputtering them with gold/palladium alloy. The average size and the size distribution of dispersed lignin particles were determined by image analysis.

Results and discussion

The results are presented in several sections. The composition dependence of selected properties is shown in the first followed by the effect of lignin content on the structure of the blends prepared from the various polymers. The load bearing capacity of dispersed lignin particles is discussed in the next section, and eventually the detailed analysis of miscibility-structure-property correlations is presented in the final section of the paper.

Properties

The properties of polymer blends are influenced by several factors including the miscibility of the components. The strength of interactions, compatibility and miscibility are often deduced from the composition dependence of various properties, the most often mechanical characteristics, modulus or strength. The effect of lignin content on the stiffness of the blends is presented in **Figure 1** for all the studied blends. Modulus is increasing with lignin content in each case and even the extent of increase is practically the same for the various polymers, except maybe for PP. In this latter case, the increase is somewhat smaller with increasing lignin content than in the rest of the polymers. The stiffness of the matrix polymers covers a relatively wide range, from 0.4 GPa for the ionomer to about 3.6 GPa for PLA. The stiff aromatic structure and the strong self-interaction of the lignin molecules result in very stiff particles and in the increase of the modulus of blends containing them. However, the results do not give any information about either the strength of interactions or the miscibility or compatibility of lignin and the matrix polymers.

The tensile strength of the blends is plotted against lignin content in **Figure 2**. The interpretation of the correlations is even more difficult than in the case of stiffness. The most diverse composition dependence is observed for the various polymers from continuous decrease (PP, PLA), through correlations exhibiting a maximum (PS, PMMA, PC, PETG) to a more or less continuous increase with lignin content (ionomer). The decrease of strength is often interpreted as weak interaction and immiscibility, while an increase as strong interaction and good compatibility. In this simple scheme, correlations with a maximum cannot be interpreted or they are difficult to explain. However, because of the effect of several factors, the direct interpretation of primary data is very difficult or impossible. The composition dependence of properties measured at large deformation (yield properties, strength) is affected by the characteristics of the matrix, interactions and structure as well.⁴⁵⁻⁴⁸ Consequently, the strength of interactions or miscibility cannot be judged

from the data presented in **Figure 2**, further analysis is needed.

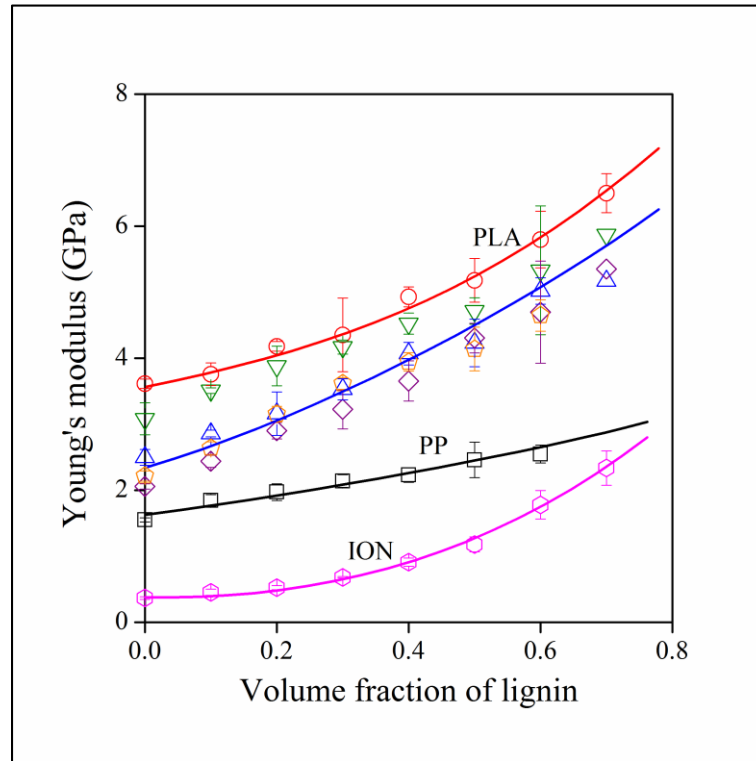


Figure 1. Composition dependence of the stiffness of polymer/lignin blends. Matrix polymer: (□) PP, (○) PLA, (△) PMMA, (▽) PS, (◇) PETG, (●) PC, (●) ionomer.

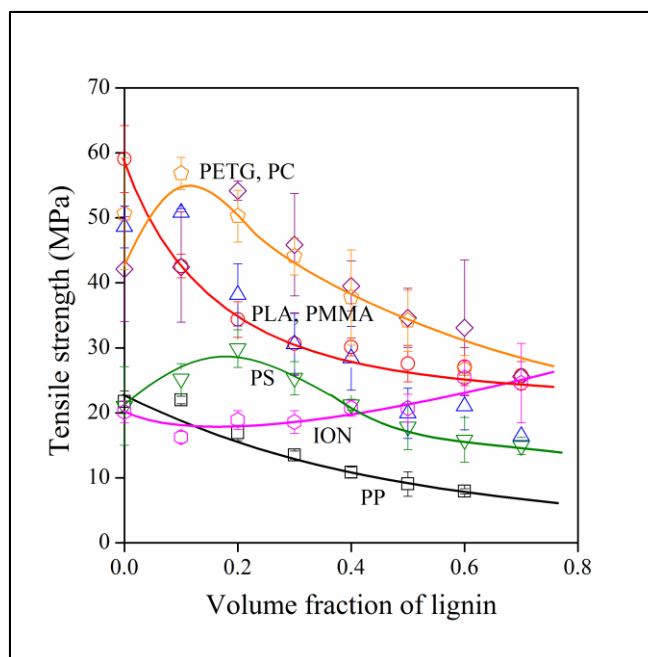


Figure 2. Effect of lignin content on the tensile strength of polymer/lignin blends. Symbols are the same as in Figure 1.

Deformability is an important attribute of all structural materials, because it is often closely related to impact resistance. The deformability of the matrix polymers and that of the polymer/lignin blends studied varies in a relatively wide range at small lignin contents, but invariably decreases with as the amount of lignin in the blend increases (see **Figure S2** in Supplementary Information). The elongation-at-break values of the ionomer/lignin blends are reasonable up to 30 vol% lignin content, but most of the blends are quite stiff and break at very small deformations. This is one of the drawbacks of these blends, which may hinder their practical application.

Structure

Miscibility and homogeneous structure were reported in the literature for the blends of the most diverse polymers and lignin,^{19,20,27,33,40-42} but the claims were not supported by experimental evidence in many cases. The lignin used in our experiments is a commercial product prepared by

spray drying. Its particle structure is presented in **Figure 3a**. The average size of the particles is around 80 μm . The structure of some of the blends is demonstrated by further micrographs in **Figure 3**. Large particles can be seen in PP (**Figure 3b**), but they are much smaller than the original lignin particles. Obviously the original particles break up during processing and form smaller droplets in the matrix polymer. The average size of the dispersed lignin particles depends very much on the type of the polymer used as matrix, and very small, several tenths of a micron sized particles form in the ionomer (**Figure 3e**). The composition dependence of the average particle size is presented in **Figure 4**. Large particles develop in PP and PLA, and much smaller in the rest of the polymers. The extent of changes with lignin content also varies in a wide range, size depends only slightly on composition in most of the polymers, except in PP and PLA.

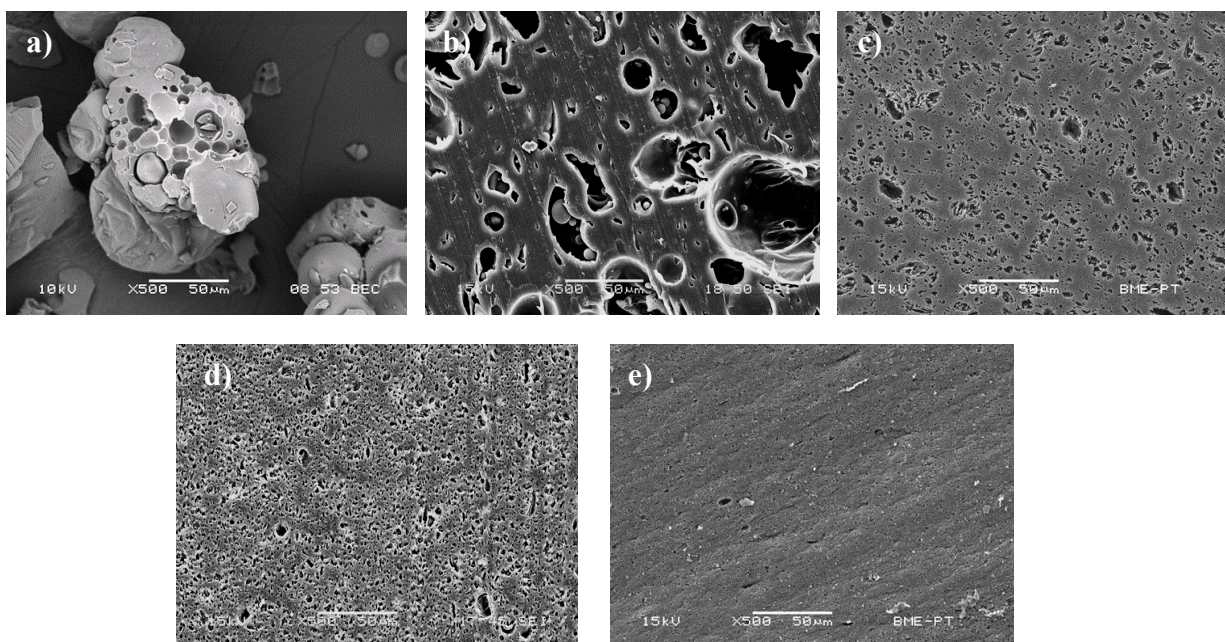


Figure 3. Influence of the chemical structure of the matrix polymer on the size of dispersed particles in polymer/lignin blends. Lignin content: 20 vol%. SEM micrographs; lignin etched by water. a) original lignin particle, b) PP, c) PS, d) PETG, e) ionomer.

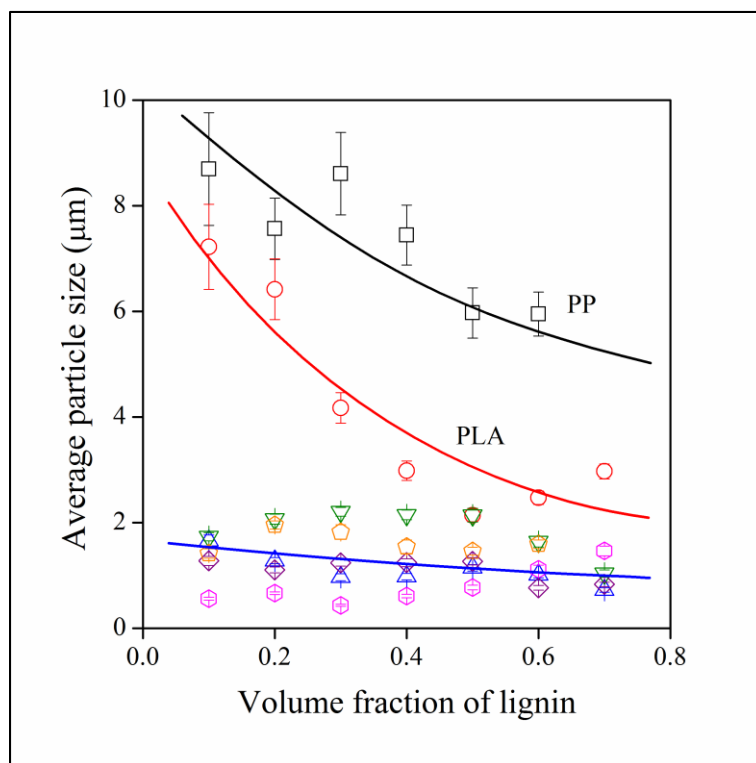


Figure 4. Average size of dispersed lignin particles plotted against composition. Symbols are the same as in Figure 1.

The size of dispersed particles in a blend are determined by thermodynamic factors and processing parameters, i.e. mainly by shear forces prevailing in the melt. Thermodynamics is determined by the interaction of the components. Shear forces depend on composition, on the amount of lignin in the blends. Our blends were homogenized in an internal mixer and the torque measured during mixing is proportional to the shear forces developing in the melt. The composition dependence of equilibrium torque is plotted against lignin content in **Figure 5**. Torque increases in all cases and with the exception of the ionomer blend, the gradient of torque increase is very similar. Shear forces are determined mainly by the viscosity of the matrix polymer, but interactions influence them as well. If processing parameters determine the size of the dispersed lignin particles, this latter should decrease with increasing torque and the extent of decrease should

be proportional to the torque measured.

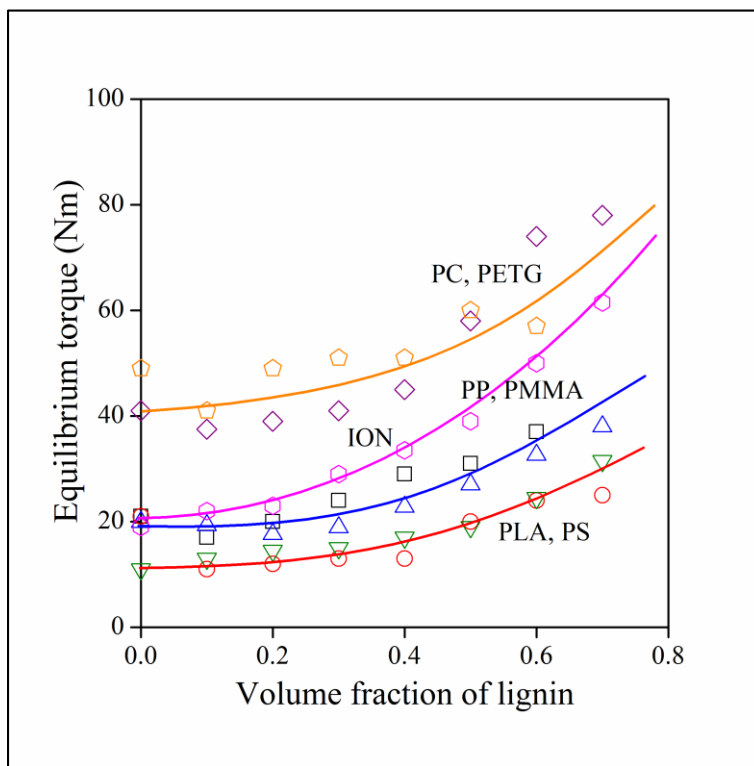


Figure 5. Changes in the equilibrium torque (shear stress) measured during the homogenization of polymer/lignin blends with increasing lignin content. Symbols are the same as in Figure 1.

Particle size is plotted against equilibrium torque values in **Figure 6**. Size decreases with increasing torque quite drastically in the PP and PLA matrix and hardly changes in the rest of the polymers. Accordingly, we can conclude that processing parameters play an important role in the determination of particle size in the two polymers and thermodynamics determines size in the others. The results also imply that interactions are rather weak between the two polymers (PP, PLA) and lignin, because processing conditions usually dominate in the absence of strong interactions. According to the results presented in this section, complete miscibility of lignin was not observed with any of the polymers studied contrary to claims published in the literature.^{19,20,27,33} Dispersed structure was observed in each case and the size of the particles

changed in a wide range, from about 10 to 0.5 μm . The differences are caused mainly by dissimilar interactions developing between lignin and the matrix polymers, but processing conditions also play a role. The estimation of interactions could give further information about structure formation and the role of interactions in the determination of blend properties.

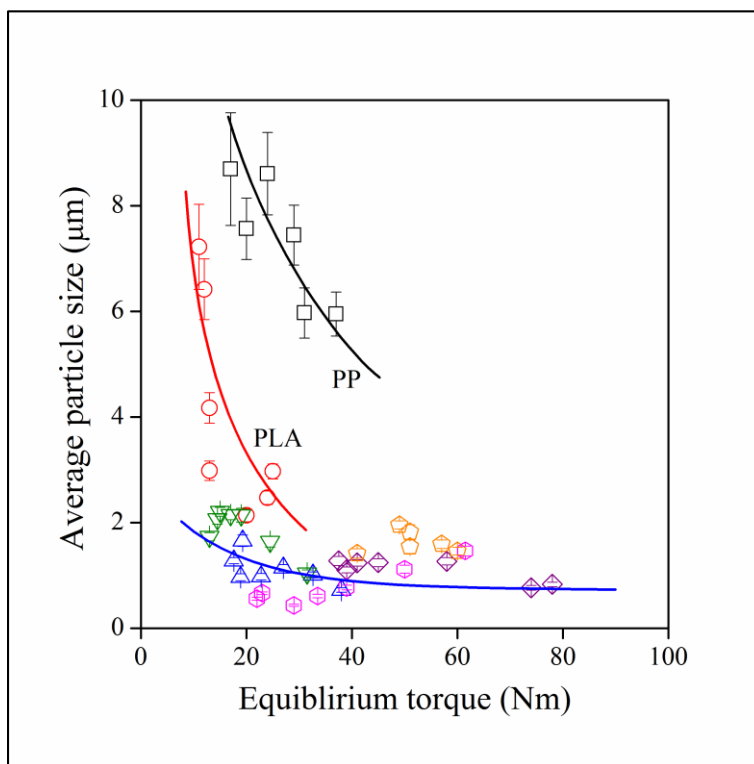


Figure 6. Correlation between the average size of dispersed lignin particles and the equilibrium torque measured during the mixing of the components. Symbols are the same as in Figure 1.

Stress transfer, reinforcement

The size of dispersed lignin particles gave some indications about the interactions developing between lignin and the matrix polymer, although particle size is influenced also by processing conditions. Interactions affect also the stress carried by the dispersed component, thus the analysis of the composition dependence of tensile strength may offer further information about them. A simple model developed earlier, which takes into account also interactions, offers the

possibility to determine interfacial adhesion quantitatively.^{45,49-51} The model describes the composition dependence of tensile strength in the following way:⁵¹

$$\sigma_{Trel} = \frac{\sigma_T}{\sigma_{T0}} \frac{1 + 2.5\varphi}{\lambda^n} = \exp(B \varphi) \quad (1)$$

where σ_{Trel} is the relative tensile strength, σ_T and σ_{T0} are the true tensile strength of the blend and the neat matrix polymer, respectively ($\sigma_T = \sigma\lambda$ and $\lambda = L/L_0$, where σ is the tensile strength, L is the ultimate and L_0 the initial gauge length of the sample), n is a parameter characterizing the orientation of the matrix, and φ is the volume fraction of the component in the dispersed phase. Eventually, B implies the relative load-bearing capacity of the dispersed and continuous phase, i.e. the extent of reinforcement. Parameter B is affected by the size of the interface between the blend components and by the properties of the interphase developing [50], i.e.

$$B = (1 + A_d \rho_d \ell) \ln \frac{\sigma_i}{\sigma_{T0}} \quad (2)$$

where A_d and ρ_d are the specific surface area and density of the dispersed component, while ℓ and σ_i are the thickness and the strength of the interphase, respectively. Both the specific surface area (which is related to the particle size of the dispersed phase in polymer blends) and the thickness of the interphase are influenced by the strength of interfacial interactions, thus parameter B can estimate component interactions.

If we transform **Eq. 1** into a linear form and plot the natural logarithm of relative tensile strength against the volume fraction of the dispersed component, we should obtain a straight line, the slope of which is proportional to the load-bearing capacity of the second component, i.e. the dispersed lignin particles, and under certain conditions to the strength of interactions. The tensile strength of the two blends with the smallest and largest reinforcing effect is plotted in this way in **Figure 7**. The correlations are linear indeed with strongly differing slopes showing dissimilar

interfacial adhesion. The B values determined are listed in **Table 2**. The values obtained cover a relatively wide range from 0.74 to 3.82. The order of the blends corresponds to previous observations, since the size of the particles was the largest in PP and the smallest in the ionomer. Accordingly, parameter B gives a good quantitative estimate of interactions. However, the results must be treated with care, since parameter B depends also on the properties of the matrix (see σ_0 in **Eq. 2**), thus always a larger B is determined in a softer matrix. Accordingly, further approach or approaches are needed to verify the results obtained by the evaluation of the composition dependence of strength.

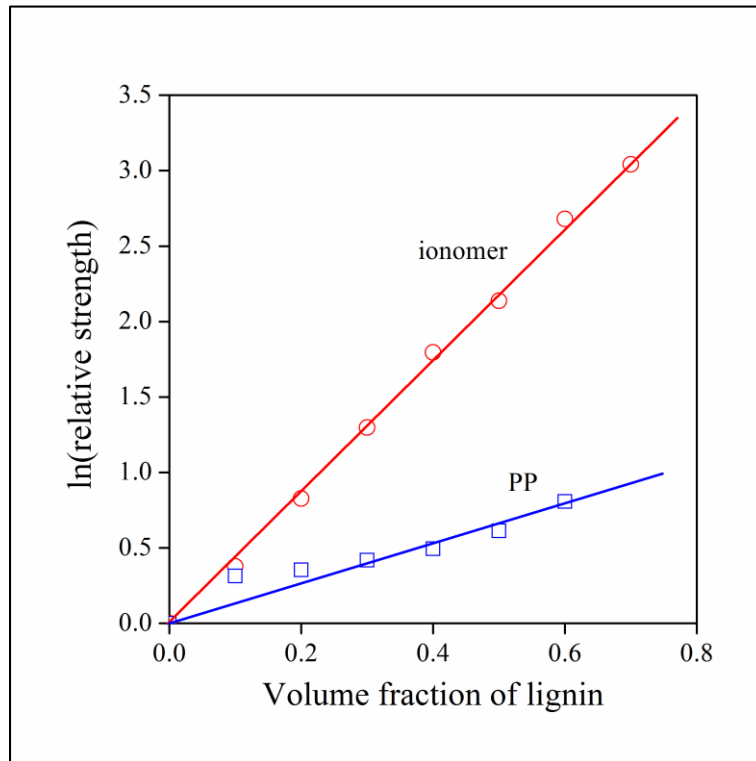


Figure 7. Relative tensile strength of two polymer/lignin blends in the linear representation of Equation 1. Symbols: (\square) PP, (\circ) ionomer.

Table 2 Reinforcing effect of lignin in the various polymers used in the study

Polymer	Matrix strength (MPa)	Parameter B	R^{2a}
PP	21.7	0.74	0.9641
PLA	59.7	1.20	0.9464
PMMA	48.6	1.55	0.9940
PS	21.0	1.68	0.9482
PC	50.6	1.48	0.9928
PETG	42.1	1.76	0.9821
Ionomer	20.2	3.82	0.9941

a) determination coefficient expressing the goodness of the fit

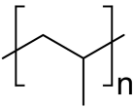
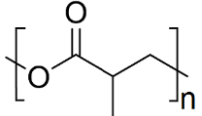
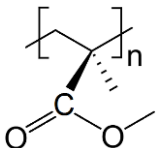
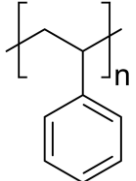
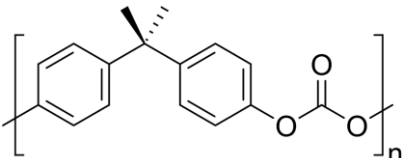
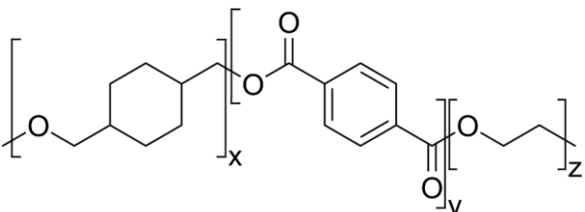
Interactions

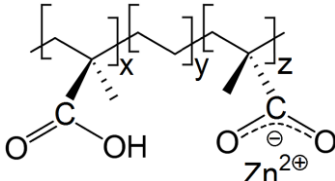
The chemical structure of the polymers used as matrix in this study covers a wide range. The polymers can form the diverse interactions with lignin and the number and strength of these interactions differ considerably as well. The structure of the polymers and the type of interactions formed are compiled in **Table 3**. Interactions are weak in the polypropylene blends generated only by weak dispersion forces. Most polymers can form hydrogen bonds, while the ionomer also ionic bonds. Since the number and strength of interactions differ considerably, we expect very different effects in the various polymers, which was confirmed by the dissimilarities in properties, but especially in structure.

The techniques used the most often for the estimation of miscibility and interactions are FTIR spectroscopy^{19,32,33,39,40,41} and the determination of the glass transition temperature of the components by DSC or DMTA.^{19,20,22-26,28,29,32,36,38,39,41,43} The shift in the wavelength of the absorbance of a characteristic band can be misleading and may not express interactions

quantitatively.¹⁰ A single T_g in a blend supposed to indicate complete miscibility, while two T_g s identical to those of the neat components imply complete immiscibility. A shift in either of the T_g values indicates the partial miscibility of the components.⁵²

Table 3 Possible interactions developing in the polymer/lignin blends studied; dispersion forces (d), hydrogen bond (H), aromatic interactions (π), electrostatic, ionic forces (ion)

Polymer	Structure	Interactions
PP		d
PLA		d, H
PMMA		d, H
PS		d, π
PC		d, H, π ,
PETG		d, H, π ,

Ionomer		H, ion
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The temperature dependence of the loss tangent of PC/lignin blends is plotted in **Figure 8**. A strong shift can be observed in the T_g of the PC phase indicating some interaction between the components. We could not detect the T_g of lignin either on the DMTA or the DSC traces thus we cannot draw conclusions from changes in its value. Interactions, or more exactly Flory-Huggins interaction parameters can be calculated from the shift in the T_g of the components by the method of Kim and Burns,⁵³ but the T_g values of both components are needed for the calculations. The most we can do is compare the shift in the T_g of the matrix polymer. These values are listed in **Table 4** and they correspond more or less to the general tendency observed before and also to the expectations. The T_g of PP does not change at all, because of weak interactions and complete immiscibility while larger changes were observed for the ionomer, PC and PETG capable of aromatic, hydrogen and ionic bonds, indicating the strongest interactions. Nevertheless, further evaluation and comparison to structure and properties are impossible with this approach.

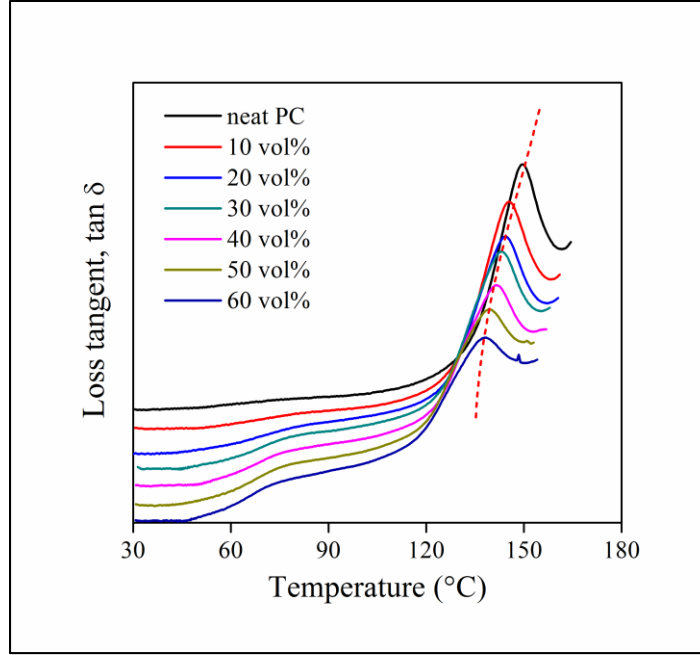


Figure 8. Considerable shift in the glass transition temperature of the PC phase in PC/lignin blends. Temperature dependence of loss tangent. Lignin content increases from top to bottom.

Table 4 Quantities characterizing interactions in the studied polymer/lignin blends

Polymer	δ^a (MPa ^{1/2})	χ^b	ΔT_g^c (°C)	B^d	$C\sigma L^e$ (MPa)
PP	16.0	11.8	0	0.74	77
PLA	19.7	7.2	+2.5	1.20	202
PMMA	18.8	8.3	−5.0	1.55	241
PC	21.0	5.9	−7.0	1.68	230
PS	18.6	8.5	−1.5	1.48	114
PETG	21.9	5.1	−6.5	1.76	480
Ionomer	27.6	1.2	+8.0	3.82	2360

a) solubility parameter, b) Flory-Huggins interaction parameter, c) difference in T_g between the neat matrix polymer and the blend at 30 vol% lignin content, d) reinforcement (see Eq. 1), stress transfer (see Eq. 7).

Structure, i.e. the size of the dispersed lignin particles changes with the type of the polymer, weaker interactions result in larger particle size. An approach to estimate quantitatively the strength of interactions is offered by the Flory-Huggins lattice theory.^{54,55} Interaction parameters can be determined, for example, from shifts in the glass transition temperatures of the components, as mentioned above, or derived by calculations. The first method cannot be used because of the lack of lignin T_g , but Flory-Huggins interaction parameters can be calculated from solubility parameters using **Eq. 3**

$$\chi = \frac{V_r (\delta_1 - \delta_2)^2}{R T} \quad (3)$$

where V_r is a reference volume with the value of 100 cm³/mol,⁵⁶ δ_1 and δ_2 are the solubility parameters of the components, R the universal gas constant and T the absolute temperature. The δ values of the polymers can be estimated using group contributions according to the approach of Small,⁵⁷ Hoy,⁵⁸ van Krevelen⁵⁹ and others.⁶⁰⁻⁶²

Flory-Huggins interaction parameters (χ) calculated with **Eq. 3** using Hoy's⁵⁸ group contribution values for δ are listed in **Table 4**. The solubility parameter of lignin was taken from the literature; it was determined experimentally specifically for a liginosulfonate sample by Myrvold.⁶³ The largest value was obtained for PP, as expected, and the smallest for the ionomer. Relatively small values were calculated for PC and PETG as well. Particle size is plotted against interaction parameters in **Figure 9** and a relatively close correlation is obtained indicating the strong effect of thermodynamics in the determination of the structure of the blends. Moderate deviations are observed in some cases (PLA, PS, PMMA), but if we consider the simplicity of the approach and the possible effect of other factors (kinetics, degradation), the correlation is very good. On the other hand, it does not help to relate interactions and structure to the properties of the

blends.

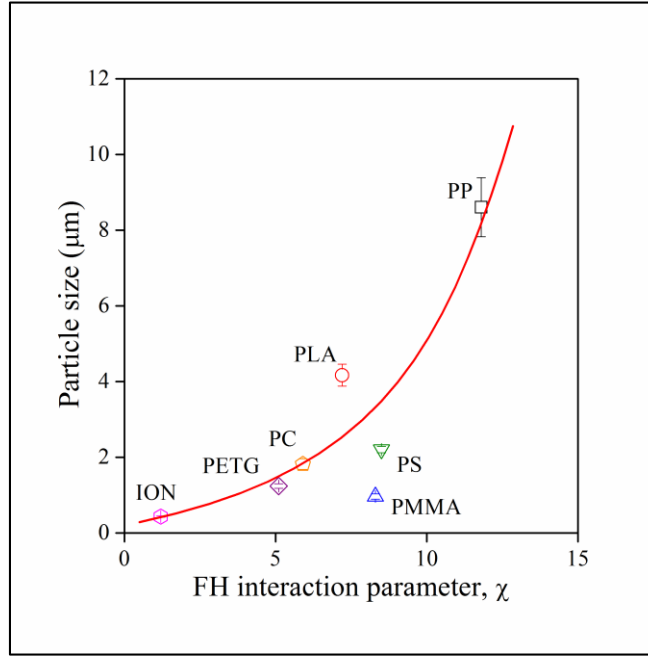


Figure 9. Correlation between the average size of dispersed lignin particles and the strength of interaction (Flory-Huggins interaction parameter, χ). Lignin content: 30 vol%. Symbols are the same as in Figure 1.

As mentioned earlier, the size of dispersed particles depend on thermodynamic factors and processing parameters, which can be expressed quantitatively by the approach of Taylor⁶⁴ and Fortelný,⁶⁵ i.e.

$$d = \frac{8 \alpha \gamma_{AB} f(\eta_{rel})}{\pi \eta_m} \varphi \quad (4)$$

where d is particle size, γ_{AB} interfacial tension, α the probability of coalescence, η_m the viscosity of the matrix, $f(\eta_{rel})$ a function of the relative viscosity of the components, the value of which is close to 1,⁶⁴ and φ is the volume fraction of the dispersed (lignin) phase. Interfacial tension can be related to the Flory-Huggins interaction parameter^{66,67}

$$\gamma_{AB} = \frac{b R T \chi^{1/2}}{V_r} \quad (5)$$

where b is the effective length of a repeat unit. Combining **Eqs. 4** and **5**, and merging several parameters into a constant leads to

$$d = k_1 \chi^{1/2} \varphi \quad (6)$$

where k_1 contains all the parameters regarded constant. **Eq. 6** relates particle size to interactions quantitatively.

The model presented in the section of *Stress transfer, reinforcement* allows us to relate properties (tensile strength) to interactions quantitatively. Parameter B expresses the load bearing capacity of the dispersed phase, but this depends also on the properties of the particles, i.e. soft particles carry less load than hard ones. Accordingly, B is related to the properties of the components through a stress transfer parameter (C),⁴⁵ i.e.

$$B = \ln \left(\frac{C \sigma_{Td}}{\sigma_{T0}} \right) \quad (7)$$

where σ_{Td} and σ_{T0} are the strength of the dispersed particles and the matrix, respectively. Stress transfer depends on the contact area between the two components (A) and the thickness of the interphase (ℓ),⁴⁵ i.e.

$$C = k_2 \ell A \quad (8)$$

where k_2 is a constant. A can be calculated from the size of the particles, while the thickness of the interphase depends on interactions; this latter correlation is expressed as⁶⁷

$$\ell = \frac{b}{\chi^{1/2}} \quad (9)$$

If we combine all the equations, we obtain the relationship between the parameter related to stress

transfer and particle size, i.e.

$$C = k_3 \frac{\varphi^2}{d^2} \quad (10)$$

The correlation between stress transfer and particle size is plotted in the representation of **Eq. 10** in **Figure 10**. Contrary to **Eq. 10**, parameter C is not plotted directly in the figure, but its value is multiplied by the strength of lignin, $C\sigma_{Td}$. This is necessary because the strength of the lignin particles cannot be determined directly. Assuming that the strength of lignin is the same in all blends, this transformation does not hinder comparison. The correlation obtained is very close as **Figure 10** shows, indicating that interactions determine both structure, i.e. the size of dispersed lignin particles, and mechanical properties, the strength of the blends.

All quantities related to interactions which were determined in this study, are listed in **Table 4**. They correlate with each other quite well with only a few values deviating from the general tendency. Considering all the assumptions made and the factors neglected, the results are quite good and allow us the drawing of conclusions about the possible use of polymer/lignin blends. We can conclude that reasonable blend properties can be achieved at strong interactions and small particle size. Practically only the ionomer meets this requirement. Moreover, the deformability of the blends is very small in most cases considerably hindering the potential application of the blends. Increasing the strength of interactions and improving the deformability of lignin by chemical modification or plasticization may lead to blends with better properties.

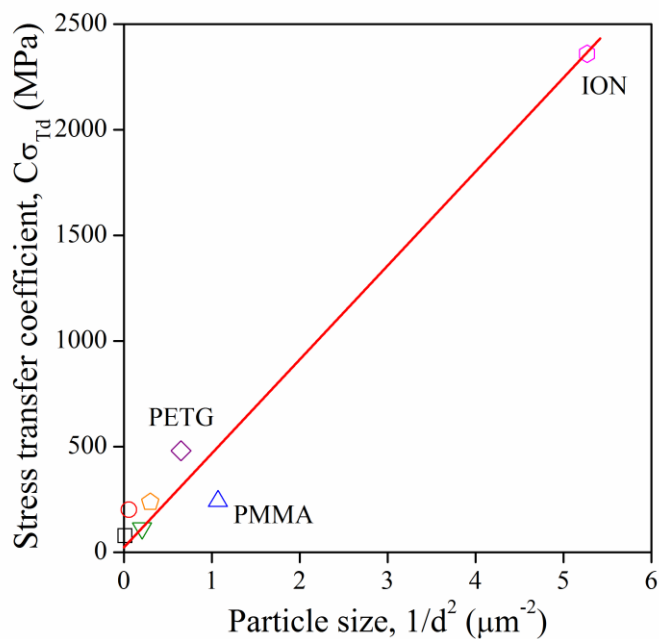


Figure 10. Correlation between the stress transfer coefficient calculated from the tensile strength of polymer/lignin blends and the size of dispersed lignin particles (see Equation 10). Lignin content: 30 vol%. Symbols are the same as in Figure 1.

Conclusions

Industrial lignin is a small molecular weight polar material in which strong self-interactions develop among lignin molecules. Its miscibility is poor with other polymers as a consequence. Heterogeneous structure formed in all the polymers used as matrix in this study, which contradicts quite a few reports published in the literature. Lignin contains various types and number of functional groups, which can enter into different interactions with other polymers as well. Only weak dispersion forces develop in polyolefins, the properties of these blends are poor. Aromatic, π electron interactions are stronger and combining them with H-bonds results in reasonable

compatibility and mechanical properties. The best properties were achieved with the ionomer as matrix in which the combination of hydrogen bridges and ionic bonds result in good compatibility and properties. The strength of interactions was estimated with the Flory-Huggins interaction parameter and good correlations were found among miscibility, structure and properties, which could be predicted with simple theories. Although blends with acceptable properties could be prepared from the ionomer and lignin, the deformability of most blends were very small limiting practical application. The plasticization or chemical modification of lignin may lead to materials which can be used in industrial practice.

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Supporting Information

Shape and dimensions of tensile test specimens. Deformability of polymer/lignin blends.

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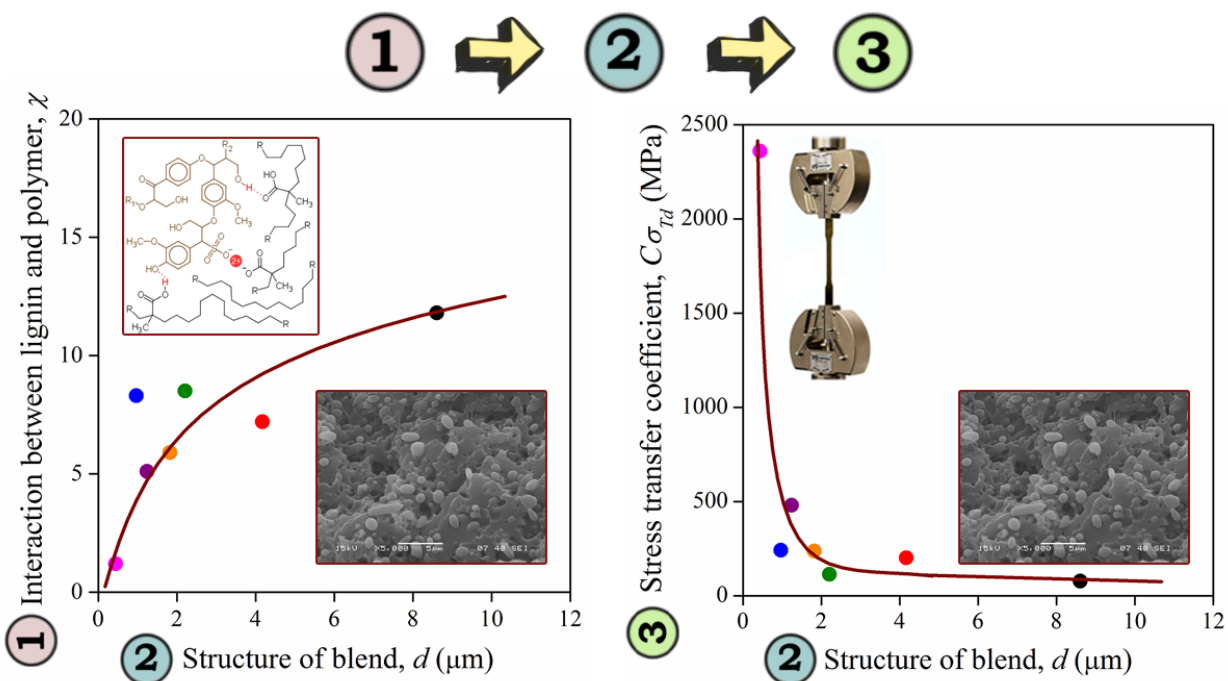
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The quantitative correlations found among miscibility, structure and properties may ease considerably the development of polymer/lignin blends in the future.